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Re: Seventh Quarterly Report #AAT-1-30620-10

Dear Martha,

This letter comprises the quarterly technical status report for subcontract #AAT-1-30620 under the High Performance Program. This report describes work performed during the seventh quarter of this contract, during April, May, and June of 2003, and covers activities performed by Global Solar Energy and by lower-tier subcontractor ITN Energy Systems.

Our goal under this program is to make very high efficiency, low-cost CIGS devices on thermally conductive substrates, as necessary for use with single-axis concentrators. The steps to be taken to achieve this goal are

- understanding and eliminating efficiency differences between the best devices on foil and the best devices on glass,
- increasing blue light collection through elimination or modification of the CdS layer, and
- demonstrating the resulting efficiency increases using a high-efficiency bell jar process.

This quarter issues relating to each of the above bullets were addressed.

1. SUBSTRATE ISSUES

CIGS depositions were underway on a variety of substrates designed to quantify and understand the effect of roughness on device performance. One series of substrates is based on very smooth, mechanically-polished, stainless steel. CIGS was deposited on the as-is steel substrate, as well as onto chemically-roughened versions of the substrate. This experimental series quantifies the effect of roughness on device efficiency. A second series of substrates was glass, mechanically treated to obtain various roughnesses, and on rough Mo foil. Fabrication of devices on this second substrate series allows separation of effects from substrate morphology from those of harmful impurity diffusion.

Devices in this study were formed by standard methods. To provide defect-passivating Na to the growing CIGS film, quantitative Na incorporation was achieved via the deposition of a 110 Å NaF precursor onto the back contact. Co-evaporation of CIGS was performed in a bell jar following the laboratory-scale three-stage batch process. Final composition and extent of the Cu-rich excursion during CIGS growth was controlled by a combination of electron impact emission spectroscopy rate monitoring and a thermopile for film emissivity monitoring. CIGS deposition area is 3” × 3”. Formation of the p-n junction was by chemical bath deposited CdS followed by sputter deposition of resistive ZnO (500Å) and 0.5 μm indium tin oxide. E-beam evaporated Ni/Al bi-layer grids completed the device structures and no anti-reflection coating was applied to the 1 cm^2 total area solar cells.

A few variations were incorporated into the CIGS depositions. As described earlier, substrates included steels of various roughnesses, rough and smooth glass, and rough Mo foil. To examine possible dependencies of roughness effects on deposition temperature, CIGS was deposited both with a 575 ^{o}C and 550 ^{o}C maximum deposition temperature. Depositions were performed both with the 3”× 3” as one continuous piece, and with the deposition area containing two 1.½” × 3” strips of different substrate material, to allow for simultaneous CIGS deposition onto a test and control piece.

Cross-sectional scanning electron micrographs (SEM) were used to examine feature size of CIGS films on various substrates. Figure 1 compares 10,000× SEM cross-sections for three different substrates. Feature sizes around 1 μm and larger are observed for CIGS on smooth glass (Figure 1a), CIGS on 700 Å chemically-roughened steel (Figure 1b), and CIGS on as-rolled Mo (Figure 1c). Feature sizes more specific than > 1 μm cannot be assigned to these samples, as a slight variation in morphology is apparent in micrographs acquired across a fracture section for steel and Mo samples, possibly due to the method used to fracture the film or actual nonuniformity. For contrast, a CIGS deposition that did not undergo a Cu-rich growth period, exhibiting much smaller feature sizes, is also shown (Figure 1d). Figure 1a and b depict bare CIGS, whereas Figure 1c and d show CIGS that has been finished into devices. Thus, the columnar-grained layer at the top of the Figure 1c and d can be identified as ITO. The Mo foil exhibits 2500 Å roughness for features larger than the CIGS grain size, as measured by stylus profilometer, and 500 Å over sub-grain size distances, as measured by AFM. Over both measurement scales, the Mo is much rougher than glass. A NaF precursor layer was utilized both on the Mo and on the steels. Because the grain size does not differ largely from one substrate to the next, it can be concluded that surface roughness does not significantly affect CIGS nucleation. This conclusion pertains to the substrate roughness and that of the NaF precursor, roughnesses measured with lateral resolution ranging from 0.1 to 100 μm, and maximum deposition temperatures from 550 to 575°C.

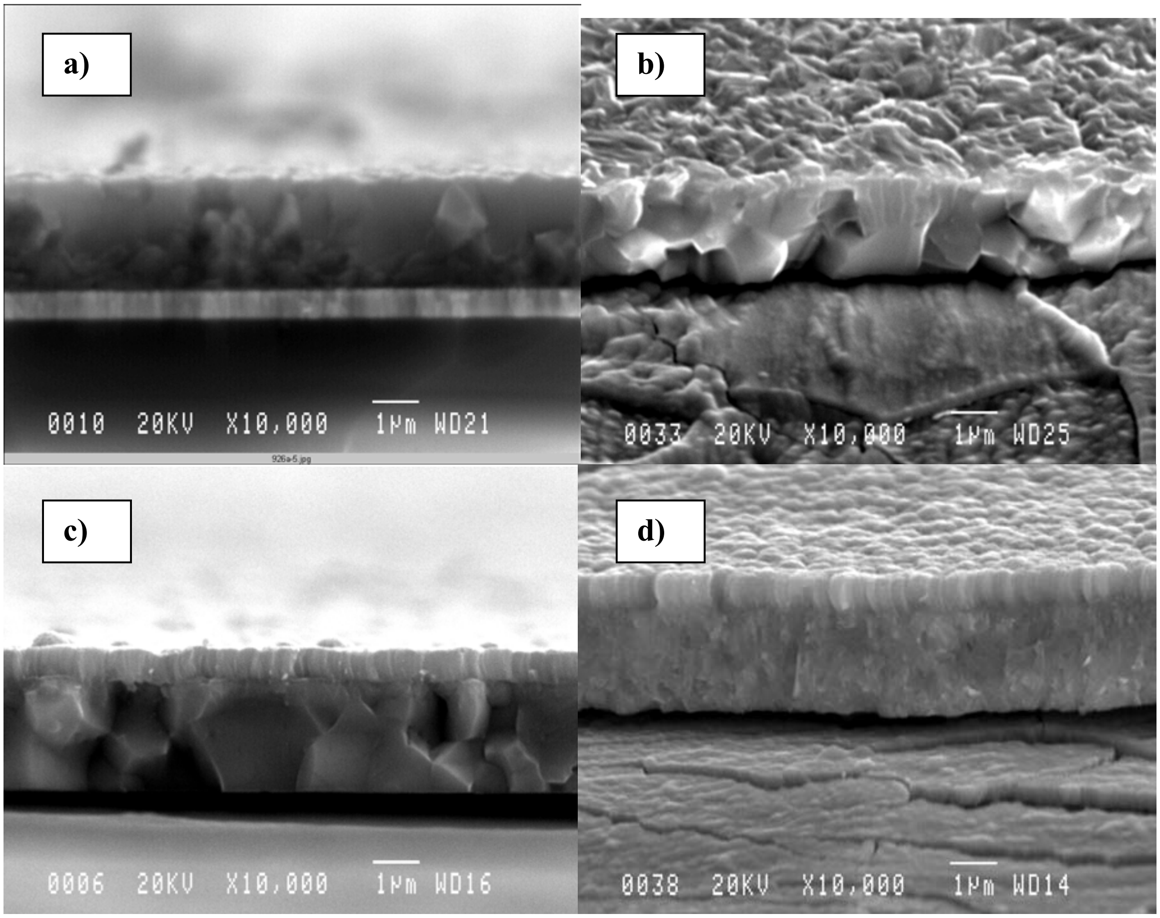

Figure 1: SEM photographs of CIGS on a) glass, b) 700Å roughness steel, c) rough Mo,, and d) 500Å roughness steel, without Cu-rich growth period.

Current-voltage parameters were measured for devices deposited on steels of various roughnesses, rough and smooth glass, and rough Mo foil. The parameters include efficiency (η), open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor (ff), and shunt resistance (r). Figure 2 shows efficiency, V_{oc}, J_{sc}, and ff as a function of substrate type and roughness. For each parameter, an "x" shows the value achieved by the most efficient device made on that substrate type during this study. The average value of the parameter over many devices is shown by the filled points. Error bars on the average parameter values are the uncertainty in the mean, based on the standard deviation of the parameter spread and the number of devices measured, assuming Gaussian statistics. Data from 154 devices and 22 substrates were used to create Figure 2. The effects of variations in 10 µm-scale roughness on average device performance for glass or steel substrates are less than experimental uncertainty. The effects are smaller than those reported elsewhere for other substrate compositions, deposition temperatures, and lateral feature size.[1]

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[1] W. K. Batchelor, M.E. Beck, R. Huntington, I.L. Repins, A. Rockett, W.N. Shafarman, F.S. Hasoon, J.S. Britt, "Substrate and Back Contact Effects in CIGS Devices on Steel Foil", *Proceedings of the 29th IEEE Photovoltaics Specialist's Conference*, 2002, pp. 719-719.

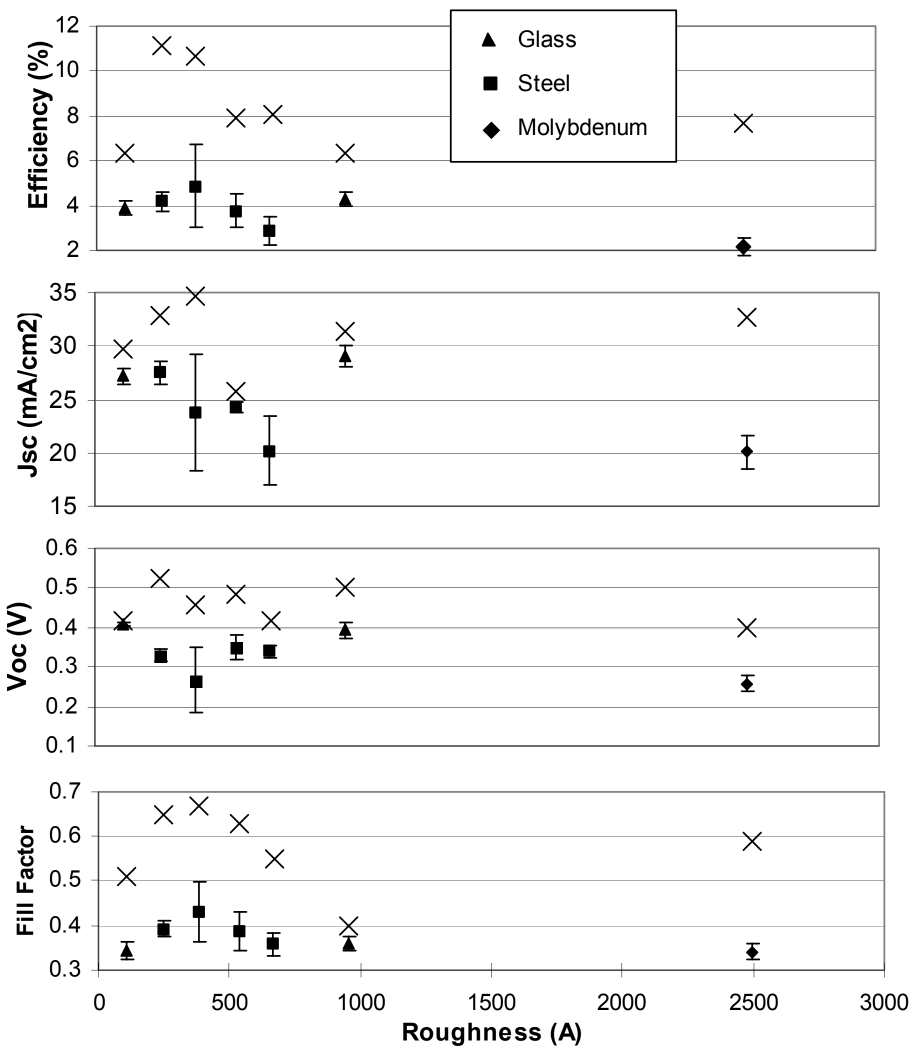

Figure 2: Average and best-device a) efficiency, b) Jsc, c) Voc, and d) ff, as a function of substrate type and roughness.

The most efficient device deposited on steel during this study yielded an efficiency of 11.1%. This performance value is typical of the results on standard glass from the bell jar utilized for this study. Surprisingly, the most efficient device deposited on glass during this study was only 6.4% efficient. As mentioned earlier, Cr, Mo, and NaF were used in the back contact on glass as well in order to provide a controlled Na amount - i.e., with the intent of providing the same back contact on glass as on foil. However, the discrepancy between the best devices on glass achieved in this study (6.4%), and standard glass or best foil efficiencies (around 11%) suggests that the Cr/Mo/NaF back contact is non-optimum on glass. One possibility may be that excessive amounts of Na have been introduced into the film via the combination of Na diffusion from the glass and Na from the NaF precursor.

It is readily apparent from Figure 2 that, for foil substrates, there are large differences between the average device parameters and those of the best device. This larger dispersion for the foil substrates can be described by the standard deviation of the parameters. Figure 3 shows the standard deviation in efficiency for the devices of the preceding figures. The standard deviation is consistently larger for devices on foil than for those on glass, despite similar average efficiencies. This combination suggests the existence of isolated defects in some of the devices on foil. Such defects may be related to metallurgical shunts or imperfect coverage by the back contact and subsequent diffusion of harmful impurities from the substrate to the CIGS.

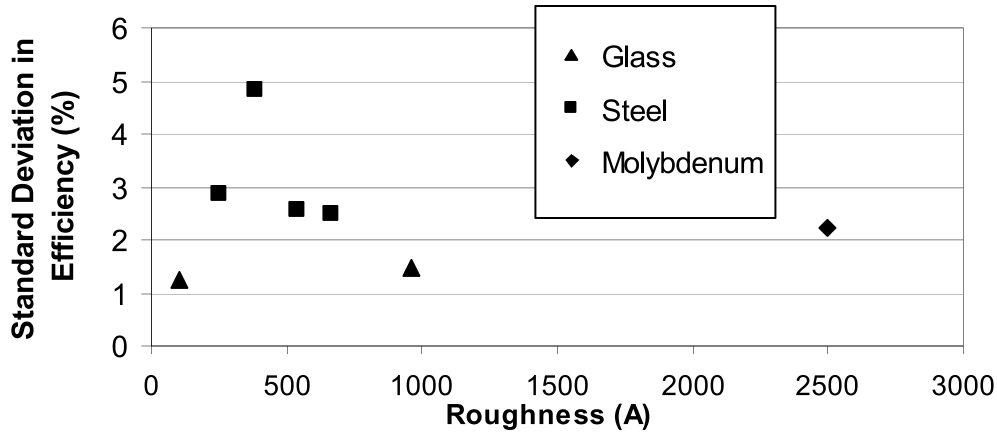

Figure 3: Standard deviation in efficiency, as a function of substrate type and roughness.

Figure 4 shows average shunt resistance for each substrate type and roughness. As in the preceding figures, error bars are based on the standard deviation of the shunt resistance and the number of devices measured, assuming Gaussian statistics. Consistent with the existence of isolated defects on foils, average shunt resistance is considerably larger for devices on glass than for those on foil. A downward trend in shunt resistance with steel roughness may exist, but is barely identifiable over experimental uncertainty.

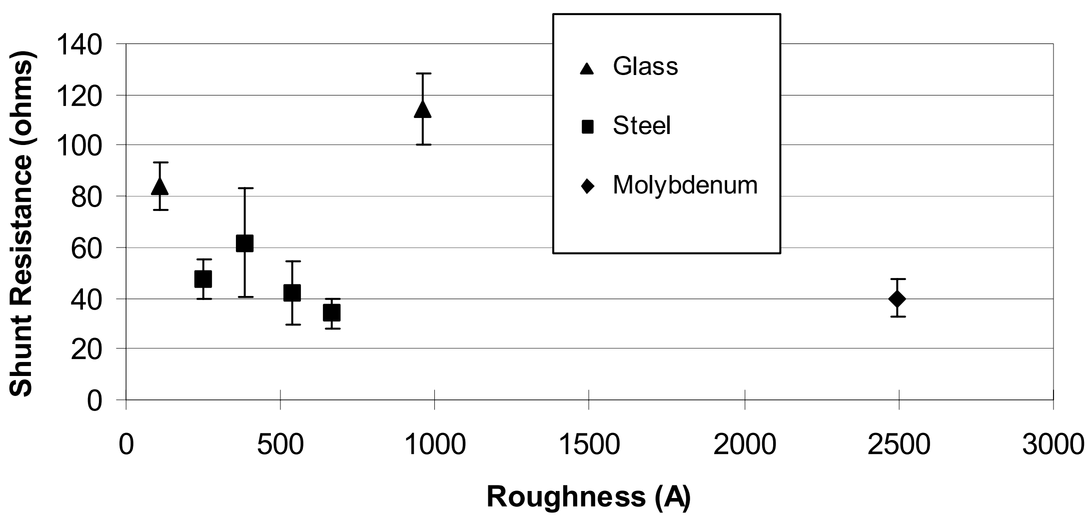

Figure 4: Shunt resistance as a function of substrate type and roughness.

Thus, several conclusions can be drawn from this quarter's work:

First, surface roughness does not significantly affect CIGS nucleation. This conclusion applies to substrates of all materials, roughnesses measured with lateral resolution ranging from 0.1 to 100 µm, and maximum deposition temperatures from 550 to 575°C.

Second, 10 µm lateral scale roughness has no measurable effect on average device performance for glass or steel substrates under these conditions. The more pronounced downward trend in efficiency with roughness reported elsewhere occurred at lower deposition temperatures or on substrates of different composition.

Third, the standard deviation in efficiency is consistently larger for devices on foil than for those on glass, despite similar average efficiencies. This combination suggests the existence of isolated defects in some of the devices on foil. Such defects may be related to metallurgical shunts or imperfect coverage by the back contact. Consistent with the existence of isolated defects on foils, average shunt resistance is considerably larger for devices on glass than for those on foil. A downward trend in shunt resistance with steel roughness may exist, but can barely be identified above the experimental uncertainty.

2. INCREASED BLUE LIGHT COLLECTION

Last quarter, a number of blue-transmissive window layers were evaluated. It was concluded is that – while CBD CdS seems to form the best junction on all absorbers studied – the success of alternate window layers is highly dependent on the CIGS properties. Partial electrolyte (PE) treatment appeared most promising, yielding efficiencies on bell jar CIS comparable to CBD CdS. However, for CIGS on flexible substrates, a highly-efficient blue-transmissive window layer was not demonstrated. It appears possible that a correlation exists between high ($\geq$ 0.95) Cu ratio and success of the PE treatment. This hypothesis is now under further investigation. Experiments are being designed to deposit CIGS films varying only the final composition. Half of each substrate will be finished into devices using CBD CdS, and the other half using PE. The extent of the Cu-rich excursion will be held constant.

3. BELL JAR BASELINE

Baseline deposition of CIGS continues to improve in small increments. Reliable composition and extent of Cu-rich excursion are now obtained on every deposition by use of improved Cu, In, and Ga rate calibration procedures for the electron impact emission spectrometer, and by using an infrared thermopile for end point detection.[2] Recent best device efficiencies are 11.8% on glass and 11.1% on steel (1 cm^2 devices, no anti-reflective coating, AM1.5 total-area efficiencies).

4. PUBLICATION DRAFT

[2] J. Kessler, J. Scholdstrom, L. Stolt, "Rapid $Cu(In,Ga)Se_2$ Growth Using End Point Detection", *Proceedings of the 28th IEEE Photovoltaic Specialists Conference*, 2000, pp. 509-512.

The study of nature of substrate roughness and its effect on device performance was assembled into a publication draft. The draft will be submitted to *Solar Energy Materials and Solar Cells* upon completion of internal review and formatting changes. A draft of the paper is attached.

Best Wishes,

Ingrid Repins

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William L. Algiene; NREL contract administrator
Carolyn Lopez; NREL contracts and business services